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DIELECTRIC RELAXATION IN RELATION TO TEMPERATURE. II

J. SOBHANADRI

PHYSICS DEPARTMENT, ANDHRA UNIVERSITY, WALTAIR

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ABSTRACT. In continuation of the previous work, the effect of temperature on the relaxation time τ of three more polar molecules in the non-polar solvent heptane was studied adopting now the Cole-Cole arc plot method for finding τ. The molecules investigated are 2, 3-dichloro nitrobenzene, 2, 5-dichloro nitrobenzene, and 6-chloro 2-nitrotoluene for which the results are newly obtained. The results are examined in the light of Eyring's theory.

In the previous paper (Sobhanadri, 1959) describing the results of experiments on the effect of temperature on dielectric relaxation in six molecules it was shown with reference to Eyring's equation

$$\tau = A/T \cdot e^{E_\tau/kT} = h/kT \cdot e^{E_\tau/kT}$$

(1) that the factor A for a given liquid remains constant and independent of temperature, (2) that its value is considerably higher than that calculated from the equation above, namely h/k, (3) that it is different for different liquids and (4) that the value of E is less than the corresponding value of $E\eta$.

These conclusions were drawn from experimental determinations of τ based on Whiffen and Thompson's (1946) method of observation at a single frequency. However, as pointed out already, it is necessary in the work of this kind to determine τ with as high an accuracy as is possible and perhaps Cole and Cole's (1941) method based on measurements at different frequencies is the most suitable. It is, therefore, thought worthwhile carrying out further investigations using this method. The purpose of this paper is to describe such investigations on the three molecules 2, 5-dichloro nitrobenzene, 2, 3-dichloronitrobenzene, and 6-chloro 2-nitrotoluene making measurements on solutions in heptane at 1 22 cm, 3.26 cm and 4.36 cm.

The experimental arrangement is the same as at 1.22 cm described in the previous paper Sobhanadri (1959). A solution of known concentration is taken in the dielectric cell. The temperature is varied between 0°C and 52°C. In order to avoid errors arising from divergences and variations in the concentration, the experimental determination of x_0, Δx and c_0 are made with the same prepared solution in rapid succession at the three wavelengths.

The values of ϵ' and ϵ'' at the different wavelengths together with the static value ϵ_0 of the solution (measured at 1 Mc/sec) are presented in Table I for different temperatures for each liquid. The plots for each substance at different temperatures are shown in Figs. 1 to 3.

It is seen that the conclusions referred to in the previous experiments are confirmed by the present results that (1) for a given liquid there is no systematic

TABLE I

(1) 6-chloro 2-nitrotoluene

Temp °C	ϵ_0	1.22 cm ϵ'	1.22 cm ϵ''	3.26 cm ϵ'	3.26 cm ϵ''	4.36 cm ϵ'	4.36 cm ϵ''	$\tau \times 10^{12}$ sec	A × 10^{11}
0	2.029	1 948	0.026	1 975	0.044	1 991	0.043	20.13	10.71
20	2.018	1.950	0 029	1 980	0 036	1.993	0.025	15.33	11.41
30	2.007	1.949	0.026	1 979	0.033	1.993	0 033	12.19	10.96
39	2.001	1.956	0 029	1.980	0.032	1.991	0.029	10 88	10.14
52	1.993	1 958	0.029	1.979	0.026	1.989	0.024	8.26	11.39
			Mean	A = 10.92×10^{-11}					
				$E_T = 1.31 \times 10^{-13}$ ergs					
				(2) 2, 3-dichloro nitrobenzene					
0	2 092	1.949	0 036	1.988	0.071	2 009	0 076	25.60	22 40
18	2 078	1.956	0.045	2 008	0 069	2.029	0 067	17.61	22 00
30	2.063	1.958	0 046	2 011	0.066	2 030	0 061	15.93	22.33
40	2.044	1.960	0.048	2.017	0.061	2.033	0.055	13 81	25.80
52	2.027	1 968	0.046	2.023	0.055	2.036	0 047	11.58	20.30
			Mean	A = 22.57×10^{-11}					
				$E_T = 1.33 \times 10^{-13}$ ergs					
				(2) 2, 5-dichloro nitrobenzene					
0	2.056	1.948	0.030	1 981	0.055	1.998	0.058	23.43	17.13
20	2.041	1.940	0.031	1.989	0.051	2.004	0.049	17.61	17.69
30	2.036	1.945	0.033	1.984	0.047	1.998	0.044	16.32	18.23
40	2 022	1.948	0 033	1.984	0 041	1.995	0.036	14.28	17.94
54	2 014	1.948	0.034	1 984	0 037	1.993	0.032	12.76	18.16
			Mean	A = 17.83×10^{-11}					
				$E_T = 1.33 \times 10^{-13}$ ergs					

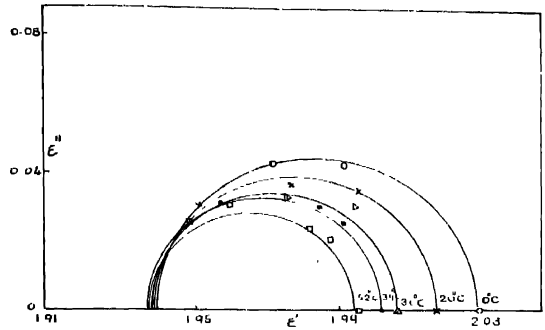

Fig 1. 6-Chloro 2-nitrotoluene.

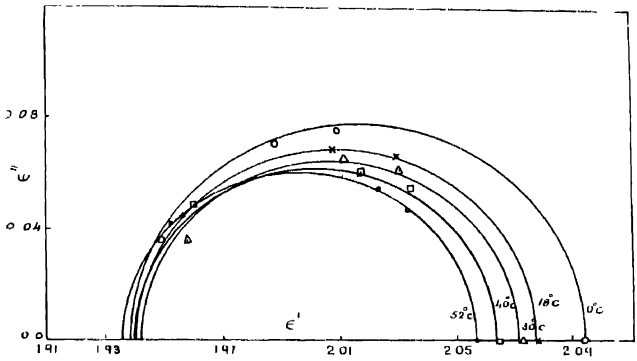

Fig. 2. 2, 3-Dichloro nitrobenzene.

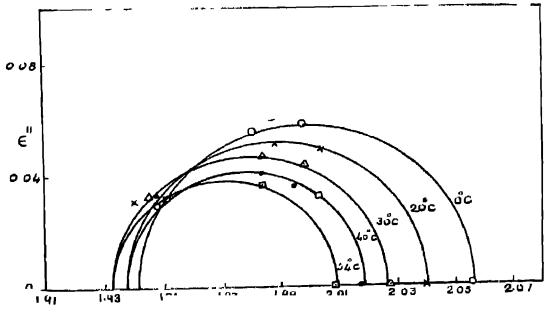

Fig 3. 2, 5-Dichloro nitrobenzene.

variation in A, its constancy may be assumed, (2) the values are considerably higher than the theoretical value 4.5×10^{-11} and (3) A is different for different liquids.

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